RECENT PROGRESS IN KINETIC MODELS
FOR COAL PYROLYSIS

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INTRODUCTION

Two mathematical models for the hypothesized kinetic
mechanisms of coal pyrolysis have attracted attention in
the recent literature. The first model uses a distributed
activation energy to simulate the pyrolysis mechanism (1-4);
whereas the second uses a set of six competitive/consecutive
reactions to model the observed results of coal pyrolysis (5).
These models have been developed to assist in the design
of improved pyrolytic reactor systems for synthetic fuel
production. They may also offer an insight into the more
complicated physical-chemical processes occuring during
hyrogasification of the coal.

The models are expected to be useful for studying two
distinct types of situations. The first type involves
the prediction of reactor performance for pyrolysis conditions
within the range of conditions studied in the laboratory.
This situation exercises the model's interpolative capability.
The second type of situation uses the model to predict
reactor performance under conditions which have not yet
been carefully studied in the laboratory. This situation
is inherently more risky, and exercises the model's pre-
dictive capabilities.

In this paper we examine the two models from the stand-
point of their interpolative and potential predictive capa-
bilities. We attempt to offer an insight into the special
set of properties which make each model attractive. More
experimental data is required before a meaningful comparison
of the two models' capabilities can be made.

MODELS EMPLOYING A DISTRIBUTED ACTIVATION ENERGY

The concept of a distributed activation energy as
originally proposed by Vand (6) was adapted to the problem
of coal devolatilization by Pitt (7), and later used by
Hanbaba and his coworkers (8), and Anthony (1-4). The model
postulates the decomposition mechanism take a large number
of independent, parallel, first order chemical reactions
with different activation energies reflecting variations
in the bond strengths of species composing the coal molecule.
Following this postulate, the rate of evolution of volatiles
V_i by reaction i is given by

$$\frac{dV_i}{dt} = -k_i \, (V_i^* - V_i) \qquad (1)$$

where $V_i{}^*$ represents the effective volatile content of the coal (1) due to reaction i, and k_i has the customary Arrhenius form

$$k_i = A_i \exp(-E_i/RT). \tag{2}$$

In Eq. (2) A_i is a constant, E_i the activation energy, R the universal gas constant, and T the temperature. The total rate of evolution of volatiles is then given by

$$\frac{dV}{dt} = \sum_i \frac{dV_i}{dt} = \sum_i - k_i(V_i{}^* - V_i). \tag{3}$$

Returning to Eq. (1) we have

$$\frac{dV_i}{V_i{}^* - V_i} = -k_i dt \tag{4}$$

which can be integrated to give

$$V_i{}^* - V_i = V_i{}^* \exp(-\int_0^t k_i dt) \tag{5}$$

Summing both sides of Eq. (5) over all reactions i we have

$$V^* - V = \sum_i V_i{}^* \exp(-\int_0^t k_i dt) \tag{6}$$

where $\quad V^* = \sum_i V_i{}^* \text{ and } V = \sum_i V_i$.

Now suppose that the fraction $V_i{}^*$ of the total effective volatile content of the coal V^* is evolved by reactions with activation energies between $E_i - (1/2)\delta E_i$ and $E_i + (1/2)\delta E_i$, so that

$$V_i{}^* = V^* f^*(E_i)\delta E_i \tag{7}$$

and $\quad \sum_i f^*(E_i)\delta E_i = 1.$ Substituting Eq. (7) into Eq. (6) we have

$$V^* - V = \sum_i V^* f^*(E_i) \exp(-\int_0^t k_i dt)\delta E_i \tag{8}$$

Finally, if the total number of parallel reactions i is large enough, Eq. (8) can be approximated by the integral equation

$$V^* - V = \int_0^\infty V^* f^*(E) \exp(-\int_0^t k \, dt)dE \tag{9}$$

where $\quad \int f^*(E)dE = 1.$

In order to make Eq. (9) mathematically more tractable, Anthony (4) assumed $f^*(E)$ to be a Gaussian distribution with mean activation energy E_0 and standard deviation σ:

$$f^*(E) = [\sqrt{2\pi}\,\sigma]^{-1} \exp(-(E-E_o)^2/2\sigma^2). \tag{10}$$

With this definition, Eq. (9) becomes

$$V^* - V = [\sqrt{2\pi}\sigma]^{-1} V^* \int_o^\infty \exp(-\int_o^t k \, dt) \exp\left\{-\frac{(E-E_o)^2}{2\sigma^2}\right\} dE \tag{11}$$

To simplify the mathematics Anthony evaluated the expression

$$[\sqrt{2\pi}\,\sigma]^{-1} V^* \int_{-\infty}^\infty \exp(-\int_o^t k \, dt) \exp\left\{-\frac{(E-E_o)^2}{2\sigma^2}\right\} dE \approx V^* - \dot{V} \tag{12}$$

numerically, choosing the adjustable parameters A, E_o, σ and
V^* so as to achieve a "best fit" with experimental data.
Although equation (12) contains only one more adjustable
parameter than that required by a single reaction model,
Anthony was able to obtain surprizingly good agreement with
experiment (4). In a recent publication Anthony and Howard
(1) attribute this agreement to the model's ability to real-
istically describe multiple decomposition reactions, such as
are supposed to occur during coal pyrolysis. However, the
following paragraphs suggest that another interpretation
of the model's success is also possible.

We first adapt the concept of a distributed activation
energy to systems of equations describing irreversible chem-
ical reactions such as the Reidelbach-Summerfield reaction
set. These equations have the general form

$$\frac{d}{dt} P_i = \sum_j X_{ij} k_{ij} R_j \tag{13}$$

where P_i is the ith product, X_{ij} are the appropriate stoich-
iometric coefficients, k_{ij} the Arrhenius rate constants,
and R_j the relevant reactants. Integrating Eq. (13) from
time $t = 0$ to $t = \tau$ yields

$$P_i(\tau) - P_i(0) = \sum_j X_{ij} \int_o^\tau k_{ij} R_j(t) dt. \tag{14}$$

Using the distributed activation energy concept, we suppose
that at time t each product has been evolved by reactions
with a distributed activation energy, so that Eq. (13) becomes

$$\frac{d}{dt} (\delta P_{ik}) = \sum_j X_{ij} k_{ijk} (\delta R_{jk}) \tag{15}$$

Integrating Eq. (15) from 0 to τ with the relation $P_i = \sum_k \delta P_{ik}$,
and the distributed activation energy hypothesis

$$\delta R_{jk} = R_j f(E_{ijk}) \delta E_{ijk} \tag{16}$$

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we have

$$P_i(\tau) - P_i(0) = \sum_j X_{ij} \int_0^\tau dt \, R_j(t) \sum_k k_{ijk} f(E_{ijk}) \, \delta E_{ijk}. \tag{17}$$

Taking the limit $\delta E_{ijk} \to 0$, Eq. (17) becomes

$$P_i(\tau) - P_i(0) = \sum_j X_{ij} \int_0^\tau dt R_j(t) \int_0^\infty k_{ijk} f(E) dE \tag{18}$$

where $k_{ijk} = A_{ijk} \exp(E/RT)$. The integral $\int_0^\infty k_{ijk} f(E) dE \equiv K_{ij}$ serves as an effective rate constant, so that Eq. (18) can be written

$$P_i(\tau) - P_i(0) = \sum_j X_{ij} \int_0^\tau K_{ij} R_j \, dt \tag{19}$$

If $f(E)$ is chosen to be the Gaussian distribution given by Eq. (10), K_{ij} becomes

$$K_{ij} = A'_{ij} \int_0^\infty \exp -\left[\frac{E}{RT} - \frac{(E - E_{ij}{}^0)^2}{2\sigma^2} \right] dE \tag{20}$$

with $A_{ij}' = A_{ijk}/(\sqrt{2\pi}\,\sigma)$ for all k. The integral in Eq. (20) can be evaluated analytically, with the result

$$K_{ij} = A'_{ij} \exp\left[\frac{-E_{ij}^0}{RT} + \frac{\sigma^2}{2R^2T^2} \right] \left[1 - (1/2)\mathrm{erfc}\left(\frac{\sqrt{2}E_{ij}^0}{2\sigma} - \frac{2\sigma}{2RT} \right) \right] \tag{21}$$

If $\sigma << E_{ij}^0$ Eq. (21) can be approximated by the relation

$$K_{ij} \approx A_{ij}' \exp\left(\frac{-E_{ij}^0}{RT} + \frac{\sigma^2}{2R^2T2} \right) \tag{22}$$

Equation (22) offers an insight into the power of the distributed activation energy concept. A graph of log k vs 1/T need not be straight in order to be fitted by the effective reaction rate K_{ij}. This is because the distributed activation energy introduces a $(T^{-1})^2$ dependence in the exponent. Thus the distributed activation energy can be viewed as a clever device for introducing a second term in the power series expansion of log k. From this one could justifiably conclude that the distributed activation energy is no more than a sophisticated curve fitting technique, as opposed to a model which offers a realistic description of the coal devolatilization process (1).

Unfortunately, Eq. (1) used by Anthony cannot be interpreted as easily as Eq. (18). If we set $\delta V^* = V_i^*$ and

$\delta V = V_i$, Eq. (1) becomes

$$\frac{d}{dt} (\delta V) = -k_i (\delta V^* - \delta V) .$$ (23)

But $\delta V^* = V^* f^*(E) \delta E$ (see Eq. (7)); hence

$$\frac{d}{dt} (\delta V) = -k_i (V^* f^*(E) \delta E - \delta V)$$ (24)

or $$\frac{d}{dt} \left(\frac{\delta V}{\delta E} \right) = -k_i V^* f^*(E) + k_i \left(\frac{\delta V}{\delta E} \right) .$$ (25)

In the limit $\delta E \to 0$ we have

$$\frac{\partial}{\partial t} \left(\frac{\partial V}{\partial E} \right) - k_i \left(\frac{\partial V}{\partial E} \right) = -k_i V^* f^*(E)$$ (26)

where $V(t) = \int_o^\infty \left(\frac{\partial V}{\partial E} \right) dE$. If we integrate Eq. (26) over E we obtain

$$\frac{d}{dt} (V) - \int_o^\infty k_i \left(\frac{\partial V}{\partial E} \right) dE = -V^* \int_o^\infty k_i f^*(E) dE$$ (27)

which compares with Eq. (1) written without a distributed activation energy:

$$\frac{d}{dt} (V) - kV = -V^* k.$$ (28)

The term $\int_o^\infty k_i f^*(E) dE$ on the right hand side of Eq. (27) plays the role of k on the right hand side of Eq. (28) and may be regarded as an effective rate constant K as before. Unfortunately, the role of kV on the left hand side of Eq. (28) is played by the term

$$\int_o^\infty k_i \left(\frac{\partial V}{\partial E} \right) dE$$ (29)

and no particularly meaningful interpretation exists.

Eq. (27) governs the time evolution of the expression

$\frac{\partial V}{\partial E} \equiv V(t,E) f(t,E)$, where $\lim_{t \to \infty} f(t,E) = f^*(E)$. From this it is clear that the distribution function is not independent of time in this setting, but evolves in a manner governed by Eq. (26).

If the distribution function were independent of time, the expression $\frac{\partial V}{\partial E}$ would become $\frac{\partial V}{\partial E} = V(t)f^*(E)$ and Eq. (27) would change to.

$$\frac{d}{dt}(V) - V\int_o^\infty k_i f^*(E)dE = - V^*\int_o^\infty k_i f^*(E)dE \qquad (30)$$

For this case the integral on the left hand side of Eq. (30) could also be interpreted as an effective rate constant K, and all the preceding remarks about distributed activation energies would also be true here.

The physical meaning and implications of a time dependent distributed activation energy are not clear at the present time. It would be interesting to see if solutions to Eq. (30), which assume a time independent distributed activation energy, give better agreement with experiment than solutions to Eq. (26). In any case, certain aspects of Eq. (26) suggest that it too can be interpreted as little more than a very sophisticated curve fitting technique.

MODELS EMPLOYING A SET OF PARALLEL AND CONSECUTIVE REACTIONS

Modeling at Princeton has emphasized the development of a reaction scheme involving a set of competitive/consecutive reactions chosen to simulate observed experimental trends. The goal of this research has been the creation of a model which simulates the gross fundamental mechanisms of pyrolysis. Such a model is anticipated to have reliable predictive capabilities, as well as the more easily obtained interpolative capability.

Recent research has focused on a critical re-examination of the Reidelbach-Summerfield (R-S) model (5) for coal pyrolysis. Table I summarizes the kinetic mechanisms present in this model. A detailed discussion of the reasoning which lead to this model can be found in the literature (5). Reaction 1 was proposed to limit the decomposition of coal at low temperatures. Chemically, this step can be considered to be a reaction in which bond scissions occur and free radicals are produced. After the coal has been activated, devolatilization can proceed by two routes, depending on the heating rate and final temperature. Since tar has always been reported as being driven off first, the tar formation step was chosen to have a low activation energy. In order to satisfy the experimental observation that the gas to tar yield ratio increases with increasing temperature, the primary gas formation reaction was chosen to have a high activation energy. Reaction 4 accounts for the observation that gas evolution occurs up to 900°C during pyrolysis. Finally, reaction 5 accounts for results of the high temperature experiments of Kimber and Gray. In this

model, reactions 1, 2 and 4 constitute the low temperature
devolatilization route, and reactions 1, 3 and 5 give the
high temperature route.

Stoichiometric factors for the R-S model were chosen to
yield results which agreed with experimental data available
in the literature. Values for the activation energies and
frequency factors were obtained by fitting theoretical pre-
dictions of the R-S model to experimental data. Results
calculated using the R-S model with the stoichiometric
factors, frequency factors, and activation energies given
in Table I enjoyed good agreement with experiment. However,
the activation step employed an activation energy with a
surprizingly large value of 75 kcal/mole. Due to the magni-
tude of this number, an experimental program was undertaken
to study the activation step and to critically evaluate
the other steps in the model.

Since the activation step, by definition, cannot be
accompanied by weight loss, some other physical change had
to be measured in order to determine the reaction rate and
order. Measurements of heat release on the differential
scanning calorimeter (DSC) proved to be useful in this case,
assuming the activation step to be a single discrete reaction.
Results of several experiments (9) on the DSC indicated
that the reaction was first order with an activation energy
of 28 kcal/mole and a frequency factor of 2.0×10^8 1/sec.
Using these values, the R-S model no longer yielded results
which agreed with experiment, and further modifications
to the model were necessary.

Table 2 summarizes the modified R-S model now being
studied at Princeton. Reaction 1 describes the formation
of activated coal AC and an inert solid S_1. The activated
coal may be viewed as a viscous liquid bitumen, which exists
in equilibrium with a polymerized solid S_2. The activated
coal can be vaporized at low temperatures to form a gaseous
tar and an intermediate solid S_3, or it can be cracked at
higher temperatures to form a primary gas PG and another
intermediate solid S_4. Reactions 5 and 6 correspond to
reactions 4 and 5 in the original R-S model.

The differential equations given by this model have been
integrated numerically and the results compared with experi-
ment. As indicated in Fig. 1, the calculated results enjoy
good agreement with the experimental data of Badzioch and
Hawksley (10). Although this agreement is encouraging, it
cannot be regarded as providing sufficient evidence to assert
the "correctness" of the model. Evidently, at least two
models of the R-S type exist which agree with available
experimental data. There are potentially many more. In
order to determine if a "correct" reaction scheme exists
within this formalism, thus defining a model with true pre-
dictive capability, more experimental results are required.

These experiments should be designed to emphasize chemical effects and minimize the effects of heat and mass transfer. Presently, TGA and DSC studies on Wyodak coal are being made at Princeton to generate experimental rate data needed to thoroughly exercise the models discussed in this paper. Results of these studies will be reported as they become available.

CONCLUSIONS

Both the distributed activation energy model and R-S model yield results which enjoy good agreement with experiment. From this we conclude that both models have good interpolative capabilities for the limited range of experimental conditions examined to date. However, research reported in this paper suggests that the success of the distributed activation energy model may be due to its mathematical ability to fit experimental values of log k with a power series expression in T^{-1}. The predictive capability of such a model is open to question.

The R-S model represents an attempt to define a reaction scheme which simulates the gross fundamental pyrolysis reactions. If this attempt is successful, the model should enjoy good predictive capabilities. Presently, two models of the R-S type exist and both agree with experiment. It is concluded that more experimental data is required to fully exercise the models' capabilities and determine their "correctness". Experimental work to generate the required rate data is underway at Princeton and other universities.

ACKNOWLEDGEMENTS

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Table 1

General hypothetical scheme for coal pyrolysis
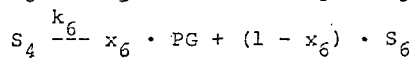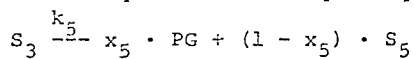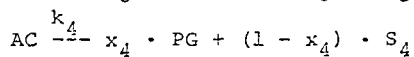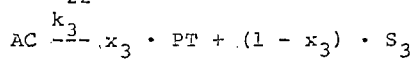of the Reidelbach-Summerfield model

$C \xrightarrow{k_1} AC$ Activation Step (high E)

$AC \xrightarrow{k_2} x_2 PT_L + (1 - x_2)S_1$ low E

$AC \xrightarrow{k_3} x_3 PG_2 + (1 - x_3)S_2$ primary decomposition   medium E

$S_1 \xrightarrow{k_4} x_4 PG_2 + (1 - x_4)S_3$ high E

$S_2 \xrightarrow{k_5} x_5 PG_3 + (1 - x_5)S_4$ high E

$AC \xrightarrow{k_6} DAC$ Deactivation Step (DAC ≠ C)

$PT_L \xrightarrow{k_7} x_7 SG_1 + y_7 S_5$ Polymerization in the liquid phase inside the particle (yields mainly solid).

$PT_L \xrightarrow{k_8} x_8 SG_2 + y_8 S_6$ Depolymerization in the liquid phase inside the particle (yields mainly gas).

$PT_L \underset{k_9}{\overset{k_9'}{\rightleftharpoons}} PT_G$ Vaporization (depending on heat and mass diffusion)

$PT_G \xrightarrow{k_{10}} x_{10} SG_3 + y_{10} S_7$ Polymerization in the gas phase

$PT_G \xrightarrow{k_{11}} x_{11} SG_4 + y_{11} S_8$ Cracking in the gas phase

where

C	=	Initial coal
AC	=	Activated coal
PT_L	=	Liquid primary tar
PT_G	=	Gaseous primary tar
PG	=	Primary gas
SG	=	Secondary gas
S	=	Solid intermediate or residue
x,y	=	Stoichiometric coefficients
E	=	Activation energy

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Table 2

Proposed Mechanism for primary devolatilization

$$C \xrightarrow{k_1} x_1 \cdot AC + (1 - x_1) \cdot S_1$$

$$AC \underset{k_{22}}{\overset{k_{21}}{\rightleftharpoons}} S_2$$

$$AC \xrightarrow{k_3} x_3 \cdot PT + (1 - x_3) \cdot S_3$$

$$AC \xrightarrow{k_4} x_4 \cdot PG + (1 - x_4) \cdot S_4$$

$$S_3 \xrightarrow{k_5} x_5 \cdot PG + (1 - x_5) \cdot S_5$$

$$S_4 \xrightarrow{k_6} x_6 \cdot PG + (1 - x_6) \cdot S_6$$
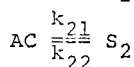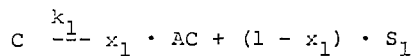
Best Fit Parameters

Reaction	x_i	Activation Energy	Pre-exponential Factor
1	0.80	28000 cal/g-mole	2×10^8 1/sec
2	1.00	4900 cal/g-mole	135
2	1.00	52000 cal/g-mole	2.6×10^{13} 1/sec
3	0.45	11700 cal/g-mole	1.24×10^4 1/sec
4	0.60	36700 cal/g-mole	5.44×10^7 1/sec
5	0.30	23000 cal/g-mole	1.30×10^6 1/sec
6	0.69	55000 cal/g-mole	1.00×10^{10} 1/sec

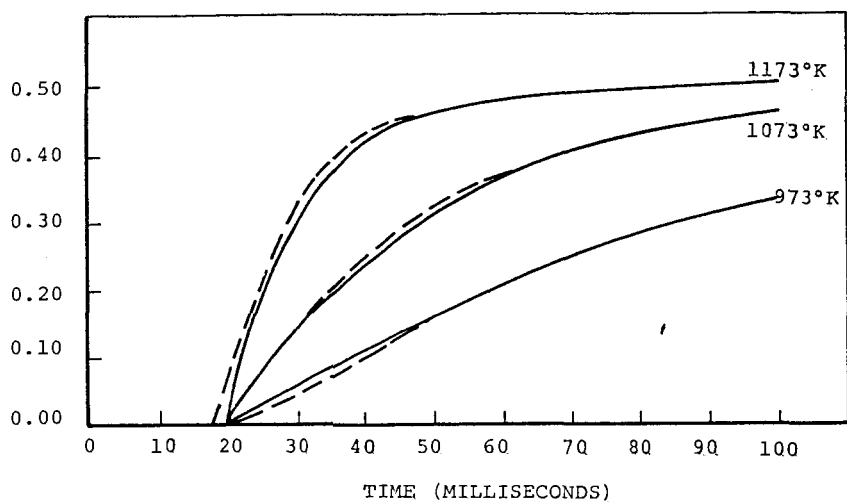|	
C	coal
AC	activated coal
PT	primary tar (volatilized)
PG	primary gas
S_i	solids
x_i	stoichiometric coefficients
k_i	Arrhenius rate constants

Figure 1   Primary decomposition of a hvAb coal at different
            temperatures as a function of time.

            --------Theoretical curve obtained with the new
                    primary decomposition scheme proposed in
                    this study.

            ————————Experimental results obtained by Badzioch
                    and Hawksley for coal D.

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